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Research Article

Method of Increasing the Fracture Toughness of Unsaturated Polyester with the Addition of Vinyl Ester as a Material for Automotive Body

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Abstract

Unsaturated polyester is the polymer material most widely used for matrix composites in the field of construction engineering, including for ships, automotive components and other engineering fields. The weakness of this polymer is that it is brittle and brittle and is unable to withstand cracking loads due to having cross-linked molecules that easily link together. The study to improve it was mixing with vinyl ester which succeeded in making the polyester crack resistant which was tested using a CTM machine and the fracture was observed using an SEM microscope. The test results showed that the polyester polymer mixed with 30% vinyl ester showed the highest increase in fracture strength, which was equal to K_{1c} = 1.67 N.mm$^{0.5}$ compared to pure polyester, only K_{1c} = 0.77 N.mm$^{0.5}$ can increase (216 %). Increasing the mixture content of 30% vinyl ester in polyester will change the brittle nature of unsaturated polyester to become more resilient because the vinyl ester molecules break the bonds of the polyester molecular chains.

Keywords

Interlock, Cross-Links, Polymer-Mixed, Fracture-Toughness, Chain-Bonds

1. Introduction

One of the uses of polyester resin is for a composite matrix with fibreglass reinforcement as the main material for the manufacture of fishing boats in Indonesia, as a substitute for wood raw materials which are increasingly scarce for the manufacture of fishing boats [1-3]. Until now, the use of boats with polyester resin composites with glass fibre reinforcement has developed very rapidly, starting from small fishing boats, speed boats, and tourist boats to vessels with a medium tonnage of 50 tons to 150 tons [3]. However, this polyester composite cannot match the advantages of wooden ships which are resistant to impacts when docked or colliding with other ships due to sea waves when the ship is docked. Polyester resin is a polymer that is brittle and stiff but has relatively good mechanical strength, is easy to print, shiny, and easy to colour, can flow into narrow gaps, and can be used as a cover or filler for empty materials [5-7]. In the engineering field, polyester resin is a material that is very much needed in the engineering field, such as for vehicles, light ship hulls, light aircraft components, and other applications engineering field [3, 6, 7]. In its application, this unsaturated polymer is brittle and cannot withstand shock loads and over a long period of use can crack and cause detrimental effects [8-10].

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This material is hard but cracks easily because the reason why this material cracks easily is because polyester resin has a covalent molecular structure with a network of cross-links and the ends of the chains are linked to each other, resulting in cross-links between the ends of the molecule. These chains that bind each other are difficult to move because they are interlocked and difficult to deform in the initial area where the crack occurs. Because at the tip of the crack, it is very difficult for there to be a plastic area, even if there is a small crack it will easily spread, causing the crack to propagate quickly and damage can easily occur [10, 11]. Due to the several weaknesses mentioned above, it limits the use of this polyester resin in structures that are subjected to impact loads or dynamic loads [12, 13]. Therefore, additional efforts are needed so that the use of polyester resin is not limited, namely efforts to prevent the chain ends of the molecules from meeting each other so that the movement of the molecules can move freely with a little free space for plastic deformation to occur [14, 15].

One way to do this is to prevent the ends of the polyester chains from meeting directly with the ends of the other polyester chains, by looking for other materials that can bond between the ends of the polyester chains. Methods of combining two or more polymers to obtain superior properties have recently developed rapidly. One of the requirements is that polymer molecules have the ends of their molecular chains bond to each other. In this research, the material that has the same hydroxyl (OH) group is the OH group of unsaturated polyester with other polymers such as vinyl ester, because they both have the same aromatic benzene atom group [8]. Previous research was carried out by adding vinyl ester to the polyester polymer to prevent the ends of the polyester molecules from merging because polyester can bond well with certainly mixed pretences, namely with 30% vinyl ester resin against the polyester resin polymer. From this research, the mechanical strength of the mixture increased by 63.6% and the length increased by 85.7% [16, 17]. The next research is to evaluate the maximum flexural fracture stress that occurs when vinyl ester is added to polyester and produces a material that has a maximum flexural fracture strength of 126.88 MPa by increasing the vinyl ester content to 30% in the polyester material and is greater than the fracture strength the stress of pure polyester just breaking is 49.71Mpa [18, 19].

To answer the need for ship construction composites as a wood replacement material, it must meet the requirements for composite materials that are resistant to fracture loads due to impact. It is necessary to identify the fracture toughness capability of adding vinyl ester polymer to polyester with different percentage ratios and dimensions of the test material. refers to testing standards crack according to ASTM D5405 standards. For this reason, in this research research will be carried out on the fracture strength of the composition of adding a mixture of polyester and vinyl ester with different mixture percentages. From this mixture, it is expected to obtain a material that has a high fracture toughness value or is termed a high fracture toughness (K_{1c}) value and also an increased area of elasticity or a large increase in strain.

2. Materials and Methods

In the main part of the discussion below, the materials needed for the research, the equipment used and the methods used for each mixture are described.

2.1. Materials

In the research, several materials are needed, such as unsaturated polyester as the main material and the mixing material is vinyl ester, then a catalyst and a diluent. Unsaturated polyester functions as a binder, making the composite a matrix because it can bind vinyl esters strongly and can close narrow gaps. The polyester used in this research is the product Polyester 1560 BL-EX by PT Kimia Alfa, SG= 1.1 g/cm^3 at 25 ℃ [8, 18].

The second material used is vinyl ester with properties that have double chemical bonds which are quite reactive with excellent chemical resistance and good flexibility. This material has a very expensive price [3] three times more expensive than polyester.

Vinyl ester purchased from P. T. AlPha Chem, brand (RYPOXY 802 EX-1, SG= 1.03 g/cm^3). The third material used in this research is methyl methacrylate often called MMA. This polymer is not rejected by the body or is biocompatible and is widely used as a biomedical material [15, 16, 20-21]. The function of MMA molecules can combine with polyester molecules, thereby reducing the stiffness of polyester. The function of MMA is to make the mixture homogeneous and evenly mixed [21, 22].

To quickly react between polyester and vinyl ester, the MEKP Epoxe a catalyst material produced by PT. Justus AlPha Chem. The catalyst functions to accelerate the rate of air evaporation and drying of the polyester and vinyl ester mixture with a percentage of 4% [9, 19, 24, 25].

2.2. Preparation and Measurement

After several of the materials above are planned and combined as described in Table 1. Then the mixture is stirred thoroughly so that it becomes homogeneous using a Vibrating pan (Daihan MSH-20D) for 15 minutes at a frequency of 20 Hz and room temperature of around 24 ℃.

The next step is to mould the material to create a crack test sample. The size of the sample to be made must follow the ASTM D 5045 standard. For this reason, it is necessary to make a mould with a length dimension of 53 mm a width dimension of 48 mm and a thickness dimension of 12 mm [26].

This study used two polymers, namely polyester resin and vinyl resin with the mixture added with MMA and MKEP

catalyst and stirred evenly. The manufacturing process is carried out by pouring a uniform mixture into the mould and then pressing it evenly with a roller or brush, this process is repeated until the required thickness is achieved. To homogenize the mixture, a vibrating stirrer was used with an amplitude of 2 mm and a frequency of 30 Hz. This stirrer is equipped with a heating plate with a heating temperature that can be set according to your wishes so that the mixed material is mixed homogeneously. Mixer equipment specifications; Brand Daihan Scientific, Model MS-H280-Pro, Operating Temperature 25– 280 [15, 19, 20].

2.3. Design of Experiment

After the sample is printed, the sample will then be tested for stretchability using a drawing machine with a CTM machine. Test specimen crack testing is standardized to ASTM D5405 with geometric dimensions shown in Figure 1. The determining factor for geometry is the ratio of the length of the crack area to the width of the crack (a/w) which is limited to between 0.45 to 0.55 and a loading rate of 2.5 mm/minute. From the dimensional ratio above, the value of the critical stress intensity (K_{1c}) can be determined which is calculated by equation (2) [22-27]

$$K_{1c} = \frac{P_Q}{Bw^{\frac{1}{2}}} . f\left(\frac{a}{w}\right) \quad (1)$$

$$f\frac{a}{w} = \frac{\left(2+\frac{a}{w}\right)\left\{0.886+4.04\left(\frac{a}{w}\right)-13.32\left(\frac{a}{w}\right)^2+14.72\left(\frac{a}{w}\right)^3-5.6\left(\frac{a}{w}\right)^4\right\}}{\left\{1-\frac{a}{w}\right\}^{3/2}} \quad (2)$$

To determine the value of the ultimate load, it can be read from the analyst on the curve of the magnitude of the load against the occurrence of displacement, and dimension B is the thickness of the test specimen. After calculating K_{1c} against the following size criteria, Equation (1).

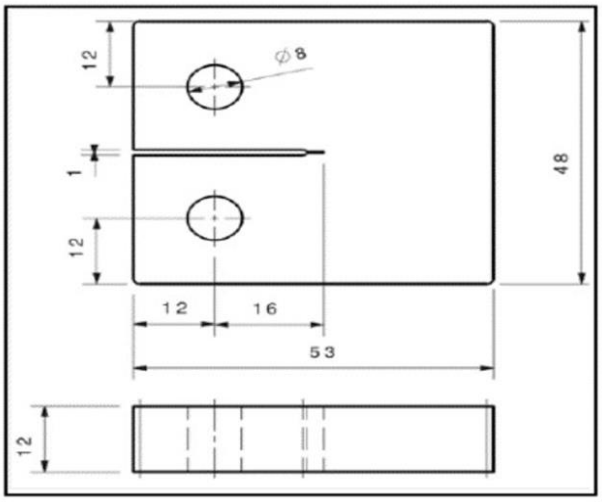
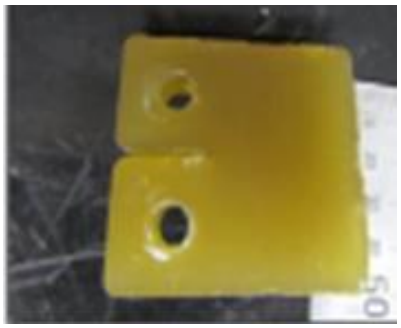
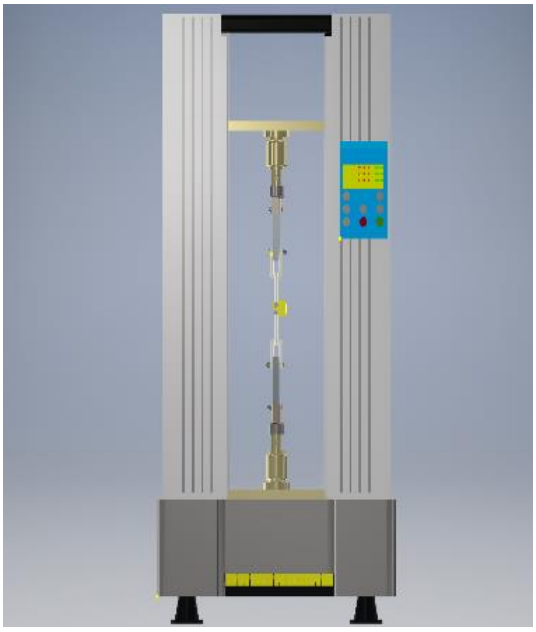


Figure 1. *The dimensions of the specimens for the crack test refer to the D5045 standard [26].*

Figure 2. *The magnetic stirrer to the mixed polymer is used for determining fracture toughness.*



(a)Printed test samples for experiments



(b) Crack testing machine (CTM) Merk Com-Ten 95

Figure 3. *The printed specimen conforms to ASTM standard D5045 (a) and CTM crack test machine (b).*

Table 1. *The specification of the material mixture composition for crack testing.*

No. \ Material	UP (%)	VE (%)
1	100	0
2	85	15
3	70	30
4	55	45

3. Results and Discussion

In the following sub-discussion, the stages obtained from the test results, analysis and interpretation of data, and things that can be concluded from the research will be described.

3.1. Fracture Surface of Morphology of Polymers Mixed

After the crack test was carried out, the shape of the flakes resulting from cracking due to the cracking load being applied until the material broke was examined under the BSE-COM FTUA SEM model [28, 29]. The crack surface of the specimen was treated with a corrosive chemical to clarify the differences in the crack surface due to stretching. The broken surface of pure polyester is shown in Figure 4(a) and the broken surface of pure polymer resin has a slightly smooth surface which shows the level of fracture pattern for material properties with low toughness or material properties that are still brittle [28]. The smooth appearance of the fracture surface (represented by the red arrow) is caused by very few breaks in the rigid chain network that reach the fracture plane which forms a line normal to the normal stress orientation due to loading and very few adjacent chains that are not rigidly connected [27-31].

Furthermore, when the vinyl ester polymer is added to the polyester, there will be crack growth which starts to get rough (which is shown by the red arrow), because some adjacent chains of polyester atoms will begin to be blocked by vinyl ester atoms which begin to bind to the polyester atoms in the atomic bonding structure. the weakest. This can be seen in areas that show fracture surfaces that differ in roughness, which indicates differences in the percentage of vinyl ester material content that is bound to the end of the polyester molecular chain. When 15% vinyl ester content is mixed with polyester, the rougher crack surface begins to appear in stripes. This is because many ends of the polyester atom chain have bonded to the end of the vinyl ester chain and the level of roughness on the fracture surface due to loading begins to oppose the movement of the load meaning that plastic deformation has begun or the level of the brittleness of polyester has begun to decrease is shown in Figure 4(b). The level of toughness of the combination of polyester and vinyl ester materials increases along with the high impact content which we immediately observe, namely 30% vinyl ester material combined with 70% polyester polymer, this indicates a break in that part maximum level of roughness or occurs on the fracture surface showing the highest toughness Figure 4(c). In Figure 4(c) a void area is formed in the presence of an unfilled mixture of the two mixtures. The surface roughness morphology shows that the rough surface is the result of plastic deformation corresponding to the highest elongation of the material. When the percentage of vinyl ester material is added up to 55%, the roughness level begins to decrease, and the number of vinyl atoms may have exceeded the saturation limit that can be bound to the polyester atoms, in Figure 4(d) [31].

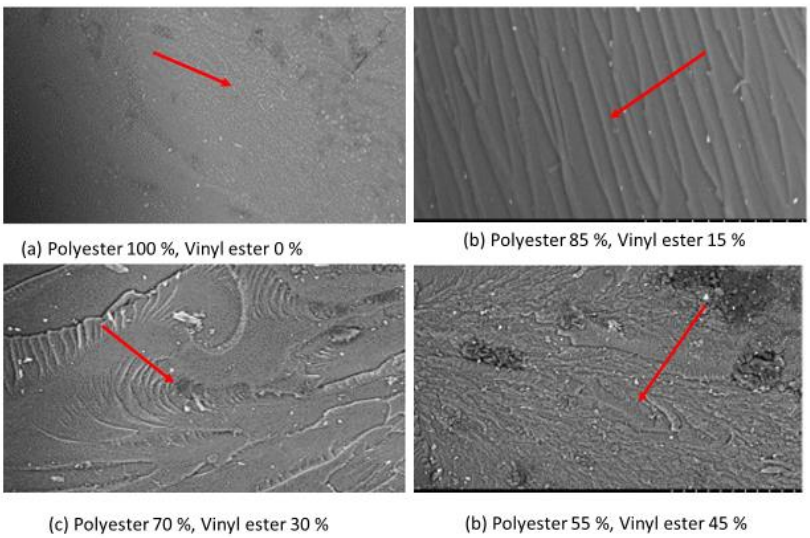


Figure 4. *The fracture surfaces for the respective UP and VE mixtures after fracture loading.*

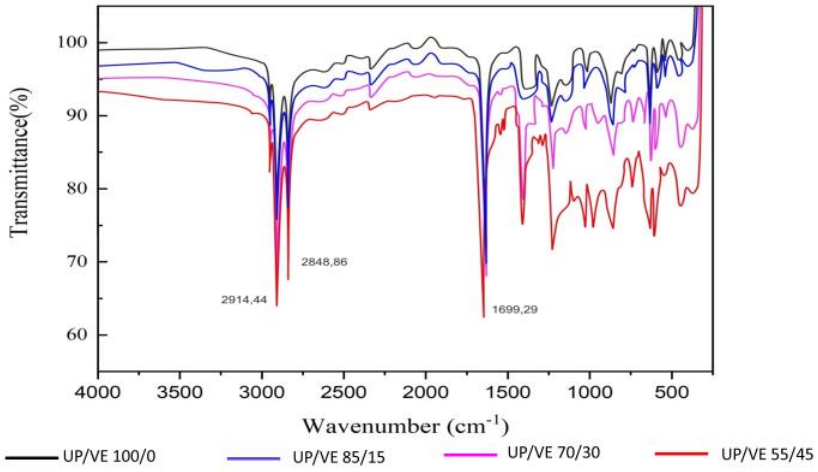


Figure 5. *FTIR curve from a blend of polyester and vinyl ester.*

Figure 5, shows the results of observing the FTIR curve of the test material, the wave peak at 1699 cm-1 is related to the substitution of the C-H atom of the benzene aromatic chain of the vinyl ester polymer. Meanwhile, the peak at 2914 cm-1 indicates the formation of long molecular chains between the polyester and vinyl ester mixture. The higher the amount of vinyl ester in the polyester mixture, the lower a different curve is formed, this means that a new polymer material is formed which is different from pure polyester or mixed polyester.

3.2. Mechanical Properties

Crack Testing Results

The crack test results for a mixture of polyester and vinyl ester materials are shown in Table 2 and the crack force magnitude curve can be seen in Figure 6 [26]. Test results on cracked specimens show that the crack propagation tends to be a straight line for brittle materials and the curve forms a curved line for hard materials [30, 15]. The shape of the curve for each mixture for the loading conditions given by the crack testing machine increases until it reaches a maximum limit which indicates that the elastic limit of the material has reached the highest level and decreases after the highest plastic limit which indicates it has reached the brittle limit. This is defined as that at the beginning of the crack load application, the energy provided by the machine in the form of material pulling force is absorbed by most of the material energy in the initial stages of crack opening, while the energy absorbed for crack propagation decreases according to the material content of the mixture. At the stage of reaching the plastic limit, crack propagation becomes faster. After pulling for cracking, the mixed polyester and vinyl ester material with a mixture containing (30% by volume) vinyl ester to polyester experienced greater elongation than pure polyester without the mixture. Some of the conditions above are caused by the load applied by the machine to break the test material starting to deflect due to interfacial adhesion in the bonded mixture of polymer, polyester and vinyl ester. To increase cracking in the material, the load is continuously increased, as shown in Figure 6. For specimens with a volume of up to 30% vinyl ester (VE) dispersed into the polyester (UP) mixture, the distribution forms evenly, but exceeding 30% the VE composition is not dispersed. well in polyester blends and the polyester begins to saturate and its fracture strength begins to decrease in the edge of the crack location and can reduce local stress concentrations and result in the polymer bearing a greater load and producing more cracks [31].

Figures 6 and 7 show the magnitude of the load applied by the tensile machine to crack the material of each crack test specimen. The tensile load from the crack testing machine to produce cracks in each test sample is shown sequentially in Table 2. The tensile load curve which increases with time until the material fails will be drawn for the sample which shows the level of resistance energy absorption strength of each mixture and can be shown in Figure 6. The crack opening load increase curve for all polymers is in the form of a straight incline at the crack initiation point, then tends to form a curve in the plastic area until it reaches the maximum peak load up to the upper plastic limit, then the load drops sharply, this indicates material settlement. strength, because the material is very brittle and failure has occurred. The maximum tensile load shows the greatest load that a cracked specimen can withstand before experiencing total failure, as shown in Table 2, Figure 6 and Figure 7. The tensile load increases with an increase in the vinyl ester mixture in the polyester polymer and the maximum cracking load occurs at 30% vinyl ester mixed with polyester, namely 367.46 N. Upon increasing the vinyl ester mixture in the polyester polymer material above 30%, the tensile load shows a decrease, this shows that not all of the vinyl ester chains are interfacially bound to the ends of the polyester chains. After initial cracking, the load decreases slowly, reflecting a decrease in material strength as the polymer matrix breaks down. The load at the peak point of the curve indicates the highest load that the specimen can resist against crack failure [2, 30].

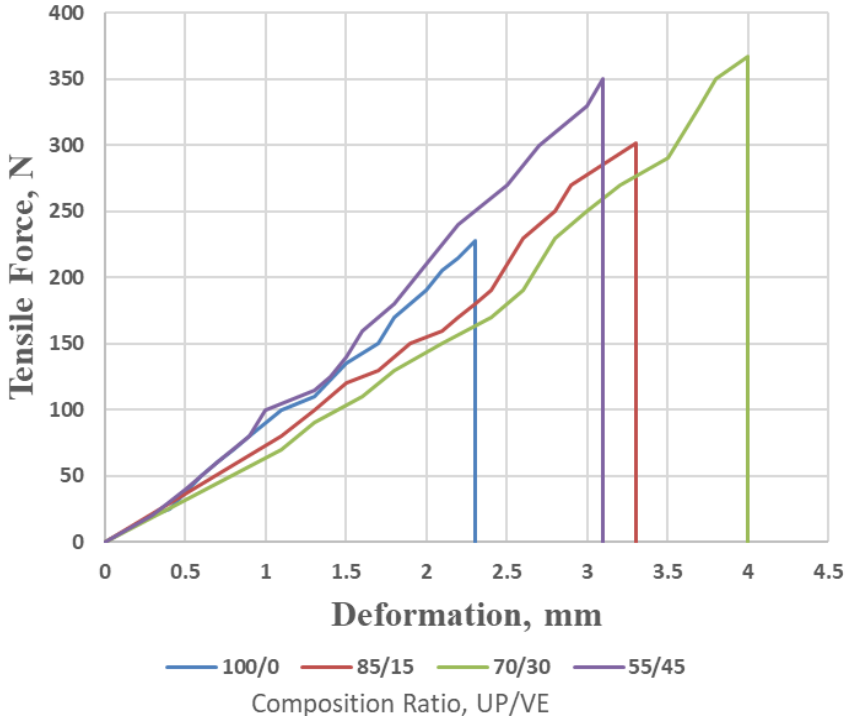


Figure 6. *The tensile force curve is given by a crack testing machine for polyester and vinyl ester blends.*

Table 2. *Tensile force curve and fracture toughness for polyester and vinyl ester blends.*

Material / No.	UP/VE (wt %)	Tensile Load, (N)	Fracture Toughness (MPa.m0.5)
1	100/0	228.34	0.77
2	85/15	302.12	0.99
3	70/30	367.46	1.67
4	55/45	350.33	1.45

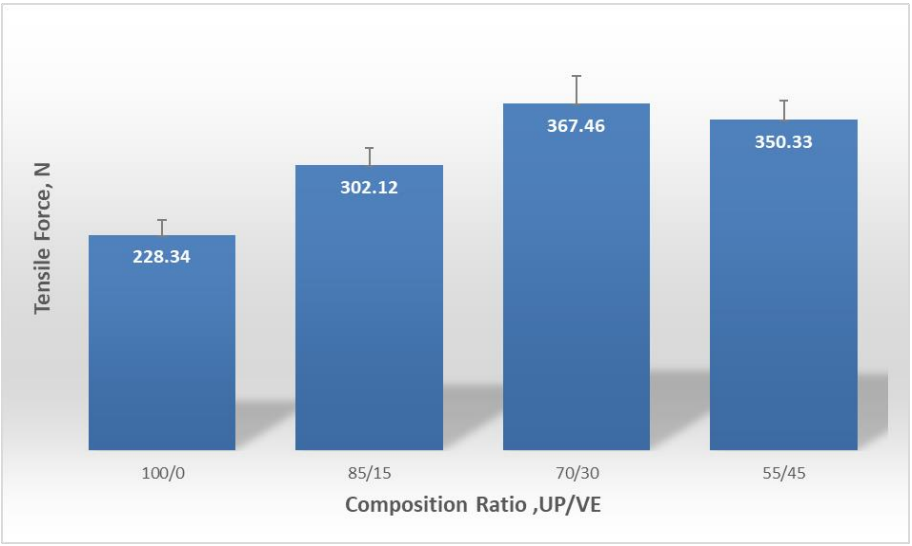


Figure 7. *The tensile force curve is given by a crack testing machine for polyester and vinyl ester blends.*

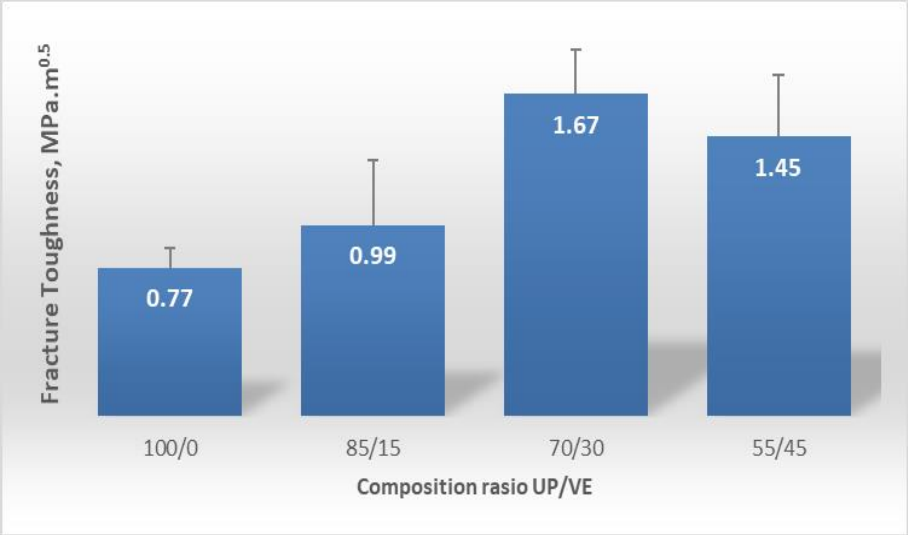


Figure 8. *Graph of the fracture toughness of a combination of polyester and vinyl ester bi-polymers.*

Energy absorption by polymeric materials is an important factor that is commonly used to assess the ability of a polymer to withstand the fracture forces acting on it. If the material can absorb greater energy to defend itself so that it does not collapse due to cracks acting on the material, then the material will be strong enough to withstand the crack load for a long time. The level of energy that can be absorbed to maintain cracks by the material is determined by the stress intensity factor which is written in Equation (1) and Equation (2) and is shown in Table 2 and Figure 8. The magnitude of the stress intensity factor from the experimental results obtained shows a strong influence on the post-crack resistance of the material, as indicated by the magnitude of the energy absorbed by the test object when subjected to a cracking load. The stress intensity factor (K_{1c}) of the moulded sample from the polymer mixture was tested against crack loads using a crack testing machine (CTM). As shown in Figure 3, the CTM specimens were made according to the standard dimensions of the crack test with ASTM D5045. The movement speed of the crack testing machine (CTM) to apply force to the sample is 2.5 mm/minute according to previous studies [27-29]. The crack-load curve obtained from the CTM crack test results for various percentages of polyester and vinyl ester mixtures listed in Table 1 is shown in Figure 6. The value of K_{1c} for unsaturated polyester mixed with vinyl ester and t will increase the value of the stress intensity factor increases for each addition of vinyl ester content until the addition of 30% vinyl ester is obtained K_{1c} = 1.67 N.mm$^{0.5}$, and after the addition of vinyl ester content of 55% of K_{1c} values decreased by only K_{1c} = 1.45 N.mm$^{0.5}$. Mixing up to 30% vinyl ester with polyester can increase the K_{1c} value which is indicated by the characteristics of a tough polymer that is resistant to cracking loads. From the results of this study, it was shown that there were several chains of vinyl ester molecule atoms that interacted directly with the ends of the polyester molecule chains so that they could disrupt the bonds between the polyester chains. This result is consistent with the rough surface morphology of the fracture as shown in Figure 4(c). The results of this study indicate that there is a successful interaction between the vinyl ester and polyester polymers and can change the brittle properties of the polyester to become more deformable up to the limit of adding 30% vinyl ester, adding above 30% in the area of adding 55% vinyl ester, the K_{1c} value drops again according to previous research [18]. Significant results show that the price of K_{1c} = 0.77 N.mm$^{0.5}$ for pure polyester can increase to K_{1c} = 1.67 N.mm$^{0.5}$ for vinyl ester mixtures up to 30%. From the research results, the addition of vinyl ester to polyester can increase the fracture toughness of pure polyester by up to 216 %.

4. Conclusions

This work reports on the successful preparation of polyester and vinyl ester blends that are resistant to impact cracking. The results of the research are related to the shape of the surface of the material tested for cracks with the CTM machine. The test results showed that the polyester polymer mixed with 30% vinyl ester showed the highest fracture strength (216%) increase compared to pure UP. The addition of 30% vinyl ester to polyester can increase the toughness properties of the polyester which results in an increase in the fracture toughness of the polyester due to the blocking of the material's polyester chain bonds from meeting.

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Conflicts of Interest

The authors declare no conflicts of interest.

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